

## In-situ Growth of Graphdiyne on Arbitrary Substrates with a Controlled-release Method

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**A versatile controlled-release method was developed for in-situ growth of graphdiyne on arbitrary substrates. Cu<sup>2+</sup>-ion escaped from the polyvinyl Pyrrolidone/copper-acetate film on the surface of various substrates (e.g. SiO<sub>2</sub>, ZnO, Al etc.), acting as the catalyst for the acetylenic coupling reaction.**

In the past few decades, feasible approaches for the preparation of all the carbon allotrope materials have been widely studied. For instance, fullerenes can be made by vaporizing graphite within a gas medium;<sup>1, 2</sup> carbon nanotubes (CNTs) have been attempted to grow with arc discharge, laser ablation and chemical vapour deposition (CVD) methods;<sup>3-5</sup> the synthesis of graphene can be via mechanical exfoliation, chemical exfoliation, chemical synthesis, and CVD methods, etc.<sup>6-9</sup> In 2010, large area graphdiyne (GDY) films were successfully fabricated on the surface of metallic copper via an in situ Glaser coupling reaction using hexaethynylbenzene (HEB) as monomer in a facile and gentle way.<sup>10</sup> GDY, which composes of hybrid sp–sp<sup>2</sup> carbon atoms and possesses the unique 2D network of benzene rings connected by diacetylenic linkages, has shown great application potential in lots of fields including battery-electrode materials,<sup>11-15</sup> gas separation,<sup>16</sup> catalysis,<sup>17-19</sup> solar cells,<sup>20, 21</sup> semiconductor devices<sup>22, 23</sup> and biological detection,<sup>24-26</sup> etc.

However, further applications of GDY in different devices are still limited by some barriers. Firstly, the growth of GDY was usually confined to metallic copper foils, which act as both substrate and supplier of the catalyst. Secondly, it is not easy to control the growing rate for GDY quantitatively. Thirdly, how to transfer the GDY onto other specific substrates and keep the fine structure undamaged is also need to be considered. Consequently, direct growth of GDY with

controllable speed on various target substrates is highly desirable. Li and co-workers<sup>27</sup> fabricated GDY nanotube arrays on aluminium oxide template, one side of which was fixed to a copper foil as the catalyst source. Liu *et al.*<sup>28</sup> synthesized GDY nanowalls on arbitrary substrates with a copper envelope as catalyst source. In these two researches, the growth conditions of GDY were greatly altered on the different substrates, although the copper foils are still used in the experiments. On the other hand, Sakamoto *et al.*<sup>29</sup> reported an excellent strategy to produce crystalline GDY nanosheets at gas/liquid and liquid/liquid interface without the use of copper foils, however, it is still a great challenge to transfer the as-prepared GDY onto the specific target substrates.

Herein, we develop a novel strategy to precisely control the release of copper-ion to govern the in-situ fabrication of GDY film on arbitrary substrates under ambient conditions. In this method, polyvinyl pyrrolidone/copper(II)-acetate (PVP/Cu(OAc)<sub>2</sub>) solution was painted onto the target substrates to form a PVP/Cu(OAc)<sub>2</sub> composite film on the surface of the substrates. When the substrates were immersed into the reaction solution, Cu<sup>2+</sup>-ions diffused slowly but continuously from the composite film into the solution, forming a concentration gradient on the solid/liquid interface, where the acetylenic coupling reaction took place catalysed by Cu<sup>2+</sup>-ions. Due to this method, the approach for GDY synthesis is called as “controlled-release” method. PVP/Cu(OAc)<sub>2</sub> composite film can be formed on arbitrary substrates such as SiO<sub>2</sub>, ZnO, Al etc., despite any morphology, size and texture, so it is a versatile approach for the controlled-release method for in-situ growth of GDY on arbitrary substrates. Compared with traditional method, the controlled-release approach for the preparation of GDY has some unique merits as follows: first of all, metallic copper is abandoned during the whole synthesis process, getting rid of the confine of Cu substrate and greatly reducing the cost. Secondly, the thickness of GDY can be effectively controlled by regulating the speed of Cu<sup>2+</sup>-ions release from the PVP/Cu(OAc)<sub>2</sub> film by altering the ratio of the PVP and Cu(OAc)<sub>2</sub>. Thirdly, GDY can be formed in-situ on arbitrary substrates, which offers great simplicity for the application of GDY in many ways.

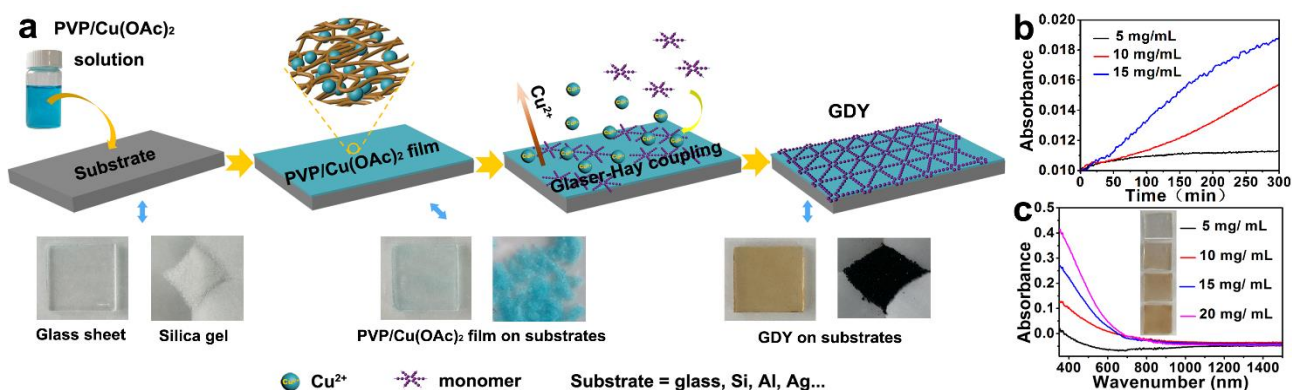
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† Electronic supplementary information (ESI) available: Experimental details and additional experimental results. See DOI: 10.1039/x0xx00000x



**Fig. 1** (a) Schematic illustration of the fabrication of GDY on arbitrary substrates with the controlled-release method and the photos of fabricating process on the glass substrate and silica gel. (b) UV/Vis spectra of  $\text{Cu}^{2+}$ -ion release from the PVP/Cu(OAc)<sub>2</sub> film in reaction solution at 350 nm. (c) UV/Vis spectra of GDY on glass sheets catalysed with a series of  $\text{Cu}^{2+}$ -ion concentration during the synthesis process. Inset shows the photos of glass sheets covered with GDY catalysed with a series of  $\text{Cu}^{2+}$ -ion concentration during the synthesis process.

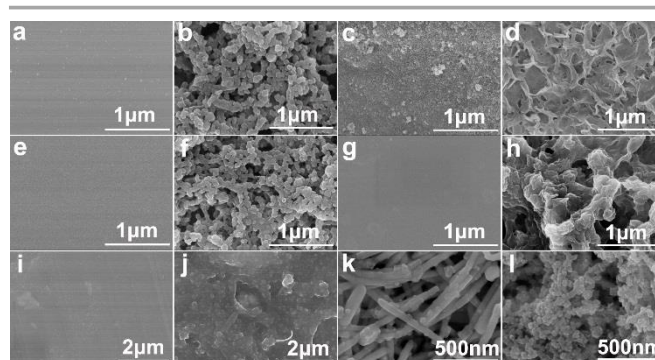
Moreover, the GDY film-based device on  $\text{SiO}_2$  wafer is fabricated to investigate the electrical property of such films, which shows that the conductivity is about  $169 \text{ S m}^{-1}$ , indicating the presence of a promising candidate of an excellent semiconductor.

The process and proposed mechanism for the synthesis of GDY on arbitrary substrates by the controlled-release method is depicted in Fig. 1. First, aqueous solution of PVP/Cu(OAc)<sub>2</sub> with different concentrations were prepared, and then the solution was painted onto the surface of target substrates (e.g.  $\text{SiO}_2$ , ZnO, Al etc.) and dried, to form a PVP/Cu(OAc)<sub>2</sub> composite film, in which  $\text{Cu}^{2+}$ -ions were restrained by the chain-like structure of PVP (Fig. 1a, inset). When the PVP/Cu(OAc)<sub>2</sub> film was immersed in acetone/pyridine ( $v:v = 20:1$ ) mixture,  $\text{Cu}^{2+}$ -ions released from the composite film with a proper speed (Fig. 1b). In the next step, the substrates coated with PVP/Cu(OAc)<sub>2</sub> film were immersed into an acetone/pyridine ( $v:v = 20:1$ ) of HEB with a concentration of 1 mg/mL for 3 days at ambient conditions to form GDY on the target substrates. The escaped  $\text{Cu}^{2+}$ -ions formed a concentration gradient and catalyse acetylenic coupling reaction at the solid/liquid interface of the substrate and the solution (Fig. 1a). Further details of the synthesis experiments are described in the experimental section of supporting information.

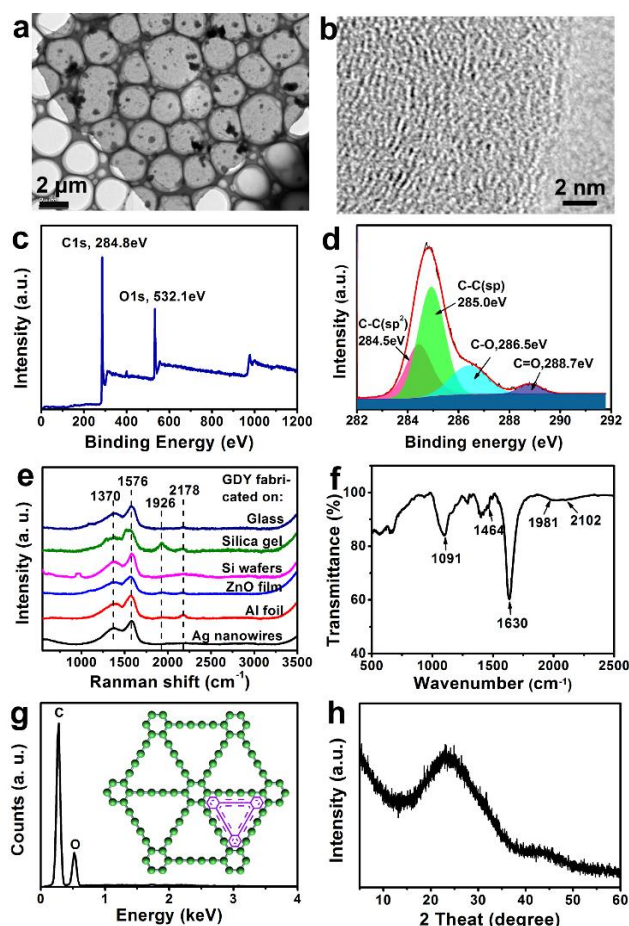
The feasibility for the controlled-release method to synthesize GDY was verified by a simple contrast experiment. Specifically, the substrates covered with and without PVP/Cu(OAc)<sub>2</sub> film were immersed into HEB solution. After the GDY synthesis process, the substrates covered with PVP/Cu(OAc)<sub>2</sub> film showed Raman spectra with four characteristic peaks of GDY, while there were no characteristic peaks of GDY for the substrates without PVP/Cu(OAc)<sub>2</sub> film (Figure S 1). This confirm the feasibility of the controlled-release method for the in-situ preparation of GDY.

The release of  $\text{Cu}^{2+}$ -ions from PVP/Cu(OAc)<sub>2</sub> film in reaction solution was monitored with UV/Vis spectroscopy (Fig. 1b). In particular, a series of PVP/Cu(OAc)<sub>2</sub> solutions were prepared in which the concentration of PVP was 15 mg/mL while that of Cu(OAc)<sub>2</sub> varied from 5 to 15 mg/mL. These PVP/Cu(OAc)<sub>2</sub> solutions were spin coated on identical glass sheets at the same spin speed of 3000 rpm and time for 30 s to form PVP/Cu(OAc)<sub>2</sub> film. Fig. 1b shows the UV/Vis spectra of  $\text{Cu}^{2+}$ -ions escaping

from the PVP/Cu(OAc)<sub>2</sub> film in acetone/pyridine ( $v:v = 20:1$ ) mixture. As shown in Fig. 1b, the absorbance value increased slowly, suggesting that  $\text{Cu}^{2+}$ -ions were released with a moderate speed from PVP/Cu(OAc)<sub>2</sub> film. More remarkably, the larger the concentration of  $\text{Cu}^{2+}$ -ions in PVP/Cu(OAc)<sub>2</sub> solution when forming PVP/Cu(OAc)<sub>2</sub> film, the higher is the releasing rate of  $\text{Cu}^{2+}$ -ions from PVP/Cu(OAc)<sub>2</sub> film. Due to the altering of the releasing rate of  $\text{Cu}^{2+}$ -ion which acted as a catalyst for GDY synthesis, the thickness of GDY film could be precisely controlled with this method. Fig. 1c shows the UV/Vis spectra of GDY synthesized on glass sheets using the controlled-release method with a series of  $\text{Cu}^{2+}$  concentration in PVP/Cu(OAc)<sub>2</sub> mixed solution when forming the PVP/Cu(OAc)<sub>2</sub> film. With the increase of  $\text{Cu}^{2+}$ -ions concentration from 5 to 20 mg/mL, the absorbance value of GDY enhanced accordingly, and the colour of glass sheets changed from slight yellow to brown (Fig. 1c, inset), which demonstrated that the thickness of GDY enhanced along with the increasing of  $\text{Cu}^{2+}$ -ions concentration in PVP/Cu(OAc)<sub>2</sub> solution. The reason may be as follows: when the  $\text{Cu}^{2+}$ -ions concentration in PVP/Cu(OAc)<sub>2</sub> solution increased, the ratio of  $\text{Cu}^{2+}$  and PVP in PVP/Cu(OAc)<sub>2</sub> film increased, and the releasing rate of  $\text{Cu}^{2+}$  from PVP/Cu(OAc)<sub>2</sub> film increased accordingly (Fig. 1c), which improved the concentration of  $\text{Cu}^{2+}$ -ions catalyst and enhanced the catalytic efficiency of the alkynyl



**Fig. 2** SEM images of different substrates before and after the fabrication of GDY: a, b) on glass sheets, c, d) on macro-porous silica gel, e, f) on silicon wafers, g, h) on ZnO film, i, j) on Al foil and k, l) on Ag nanowires.



**Fig. 3** (a) TEM and (b) HRTEM images of as-prepared GDY on Al foil. XPS spectra of as-prepared GDY: (c) survey scan, (d) narrow scan for the C 1s orbital. (e) Typical Raman spectra of GDY fabricated on different substrates. (f) FTIR and (g) EDS spectrum of GDY. Inset is the structural representation of GDY. (i) XRD patterns of as-prepared GDY.

coupling reaction when GDY was synthesized. The thickness of GDY grown on  $\text{SiO}_2$  can also be regulated using this method (Figure S4).

Using this method, GDY was fabricated on various substrates with diverse dimensions and features, such as on insulators, semiconductors and conductor. Fig. 2 shows the SEM morphology of the target substrates before and after fabrication of GDY. For the initial substrates (Fig. 2 a, c, e, g, i, k), the surface was relative smooth and clean, while after the acetylenic coupling reaction, the surface appearances of the supports changed significantly, exhibiting uniform and continuous films on the surface of each substrate (Fig. 2 b, d, f, h, j, l), which indicating the successful building of GDY. Fig. 2a-d indicates that GDY was successfully fabricated on insulating substrates of glass and macro-porous silica gel. GDY fabricated on flat glass sheets exhibits particle morphology (Fig. 2b), while those fabricated on macro-porous silica gel seem loose and porous (Fig. 2d). Fig. 2e-h shows that GDY was well built on semiconductors of silica wafer and ZnO film. GDY on Si wafer presented a similar particle morphology as glass sheets, while GDY grown on ZnO showed a bigger particle morphology. Fig. 2i-l displays that GDY was successfully fabricated on conductor substrates of Al foil and Ag nanowires. It was observed that the

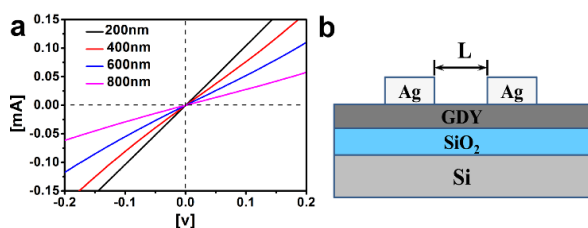
GDY film on Al foil had a more compact structure compared to GDY grown on other substrates. The GDY on the surface of Ag nanowire also show a granular appearance. The growth of GDY on the surface of Ag nanowire formed a perfect metal-carbon core-shell nano structure, giving an application potential in the field of catalyst. Besides, using the controlled-release method, GDY can also be well fabricated on the substrates of ITO glass, nano-layered montmorillonite and  $\text{SiO}_2$  wafer (Figure S2, S3). The diverse morphology of GDY on various substrates may be resulted from the different wettability of PVP/Cu(OAc) $_2$  solution on as well as the surface structure of different substrates. Overall, GDY can be directly fabricated on insulators, semiconductors and conductor substrates with arbitrary dimension and appearance, which offers unexpected convenient for the fabrication of various devices.

The morphology of GDY was further observed by TEM. Fig. 3a shows the TEM image of as-prepared GDY grown on Al foil, which indicates the GDY sheet to be a semi-transparent and continuous film, with a flat and uniform smooth surface. High-resolution TEM (HRTEM) was also employed, which revealed that the layer-to-layer distance of GDY sheets is 0.365 nm (Fig. 3b), coincident with previous reports.

The structure and elementary composition of as-prepared GDY were studied systematically with X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Powder Diffraction (XRD). The survey scan of XPS in Fig. 3c displayed unambiguously that the GDY were composed of main elemental carbon and a small amount of oxygen, which was in accordance with the EDS analysis (Fig. 3g). The presence of oxygen might come from the absorption of oxygen from air as well as the oxidation of some terminal alkyne.<sup>10</sup> Fig. 3d presents a high resolution asymmetric C 1s XPS spectrum of GDY. The C 1s peaks of GDY could be deconvoluted into four main sub-peaks at 284.5, 285, 286.5 eV and 288.7 eV, which could be assigned to orbitals in C-C ( $\text{sp}^2$ ), C-C ( $\text{sp}$ ), C-O and C=O bonds, respectively.<sup>10, 11</sup> The area ratio for the signals of the  $\text{sp}$ - and  $\text{sp}^2$ -hybridized carbon atoms was 2, which was in good agreement with the chemical composition of GDY. The atomic-scale map of GDY was exhibited in the inset of Fig. 3g.

Fig. 3e shows the Raman spectra of as-prepared GDY on several substrates. Four peaks at around 1370, 1576, 1926 and 2178  $\text{cm}^{-1}$  are the characteristic peaks of GDY according to previous reports.<sup>10, 11, 13, 28, 30</sup> In particular, the peaks at around 1370  $\text{cm}^{-1}$  and 1576  $\text{cm}^{-1}$  correspond to the breathing vibration of  $\text{sp}^2$  carbon domains (D band) and the first-order scattering of the  $\text{E}_{2g}$  mode for in-phase stretching vibration of  $\text{sp}^2$  carbon lattice (G band) in aromatic rings, respectively. Other two weak vibration peaks at about 1926 and 2178  $\text{cm}^{-1}$  were contributed to the vibration of conjugated diyne links. Furthermore, FTIR spectrum of the as-prepared GDY film grown on Al foil was also investigated in Fig. 4f. The band observed at 1091  $\text{cm}^{-1}$  could be attributed to the stretching vibration of C-O bond. The peaks located at 1464  $\text{cm}^{-1}$ , 1630  $\text{cm}^{-1}$  can be assigned to the skeletal vibrations of aromatic ring, and the wide bands at 2102  $\text{cm}^{-1}$  are due to the typical C-C triple bond stretching vibration.<sup>30</sup> The XRD data in Fig. 3h showed wide peak of C (002) of the as-





**Fig. 4** (a) I–V curves of as-prepared GDY film with different thickness on devices. (b) Sketch map of GDY device.

prepared GDY which is an evidence of the presence of the amorphous nature of GDY.

The electrical characteristics of the as-prepared GDY film are investigated by recording typical current–voltage (I–V) curves. Fig. 4a shows the I–V curve of GDY film on SiO<sub>2</sub> wafers with different thicknesses, and Fig. 4b is the sketch map of GDY device. When the thickness of GDY films were 200, 400, 600 and 800 nm, the slopes of the I–V curves were  $2.9 \times 10^{-4}$ ,  $5.33 \times 10^{-4}$ ,  $8.1 \times 10^{-4}$ ,  $1.04 \times 10^{-3}$ , respectively, and the conductivity was calculated as  $163 \text{ S m}^{-1}$ ,  $169 \text{ S m}^{-1}$ ,  $167 \text{ S m}^{-1}$ ,  $181 \text{ S m}^{-1}$  accordingly. The thickness of GDY was measured by SEM (Figure S4). It is noted that although the thickness of the GDY film was different, their conductivity values were quite close, indicating that although the thickness increased, the structure and morphology of GDY was similar from bottom to top. That is to say, the as-prepared GDY was high-quality, which is one of the benefits of the controlled-release method to prepare GDY. The value of conductivity for as-prepared GDY indicated an excellent semiconductor feature, which make GDY to be a vital candidate applying in the fields of electronics, semiconductors and materials.

In conclusion, we have developed a versatile and simple strategy to fabricate GDY on arbitrary substrates with a controlled-release approach. PVP/(OAc)<sub>2</sub> film was first fabricated on the surface of substrates, then Cu<sup>2+</sup>-ions released from the film acting as catalyst for the acetylenic coupling reaction to prepare GDY. This method is working without the usage of metal catalyst and also overcome the limitations of the substrates. On the other hand, the thickness of GDY film can be effectively controlled by regulating the slow-release speed of Cu<sup>2+</sup>-ion from the PVP/(OAc)<sub>2</sub> film. The electronic property measurements of the as-prepared GDY film showed a conductivity of  $169 \text{ S m}^{-1}$ , exhibiting an excellent semiconductor feature.

This study was supported by the National Natural Science Foundation of China (21790050, 21790051, 21771187, 21603251), the Hundred Talents Program, Frontier Science Research Project (QYZDB-SSW-JSC052) of the Chinese Academy of Sciences, the Natural Science Foundation of Shandong Province (China) for Distinguished Young Scholars (JQ201610), the János Bolyai Research Scholarship of the Hungarian Academy of Sciences as well as the Hungarian Research Development and Innovation Office through grants NKFIH OTKA PD 120877 of AS.

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